The corrosion resistance of zinc-nickel composite coatings

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ABSTRACT

Purpose: The aim of this work was to estimate the corrosion resistance of composite Zn+Ni and (Ni-Zn+Ni)/Zn coatings by salt spray test, electrochemical methods and grazing incidence X-ray diffraction (GIXD) method.

Design/methodology/approach: The corrosion resistance properties of zinc-nickel coatings in 5% NaCl solution were investigated by salt spray test in 5% NaCl solution and electrochemical methods. Using Stern method the corrosion potential - E_{corr}, corrosion current density - icorr, and polarization resistance - R_p. have been determined as a measure of corrosion resistance. Phase composition of the corrosion products was determined by X-ray diffraction using Bragg-Brentano and grazing incidence X-ray diffraction (GIXD) methods.

Findings: The corrosion resistance of zinc-nickel coatings is dependent on Ni content and it grows with the increase in Ni percentage in the coatings. The higher corrosion resistance could be attributed to the presence of intermetallic Ni_2Zn_{11} phase. The maximum protective ability is reached for the coatings above 40% Ni, where the content of this phase is the highest. The results of salt spray test exhibit the appearance of white rust corrosion, which is characteristic for zinc oxidation process. The main component of corrosion products was $Zn_5(OH)_8Cl_2 \cdot H_2O$ phase. The products related to the nickel or steel substrate corrosion process were not found. The application of the GIXD technique has allowed to determine the changes in the phase composition of the corrosion products in the zinc and zinc-nickel coatings versus the penetration depth of the X-ray radiation. The presence of corrosion products on the electrode surface results in further improve in their protective ability and the limiting of the corrosion processes.

Research limitations/implications: Special attachment for GIXD technique is required for the experiment.

Practical implications: The zinc-nickel coatings could be applied as protective coatings for steel substrates.

Originality/value: The application of GIXD technique allows to determine the chemical composition of corrosion products along the coating thickness.

Keywords: Zinc; Nickel; Composite coatings; Corrosion resistance; GIXD technique

1. Introduction

The Zn coated materials are characterized by higher corrosion resistance in aggressive environment [1-3]. In order to enhance the corrosion resistance of zinc coatings their surface properties should be improved. Thus, Zn-based alloy coatings containing metals such as: Ni, Co, Fe have been developed. However, electrodeposition of such alloys exhibits an anomalous character resulting in a higher amount of Zn in the obtained deposit. Another option is to plate Zn+Ni composite coatings with

mentioned iron-group metals in a form of powder [4-5]. Thermal treatment of such obtained coatings leads to the homogenization of their components through the creation of intermetallic compounds or solid solutions. The percentage of nickel should be critical for establishing the higher corrosion resistance of such obtained coating.

The aim of this work was to estimate the corrosion resistance of composite Zn+Ni and (Ni-Zn+Ni)/Zn coatings by salt spray test, electrochemical methods and grazing incidence X-ray diffraction (GIXD) method.

2. Experimental

The subject of this investigation were Zn+Ni and Ni-Zn+Ni/Zn composite coatings. Zn+Ni composites were deposited under galvanostatic conditions on S235JR steel substrate from a zinc chloride bath in which nickel powder was dispersed by stirring. Chemical composition of the electrolyte and the conditions of the deposition process are described in our previous works [4-5].

Ni-Zn+Ni/Zn coatings were obtained on the St3S substrate by chemical reduction of zinc and nickel ions from sulphate bath containing dispersed nickel powder and next the electrolytic deposition of Zn layer. The process of Ni-Zn+Ni/Zn production is described in detail elsewhere [6].

The both kinds of coatings: Zn+Ni and (Zn-Ni)+Ni/Zn, were subjected to the thermal treatment in order to acquire their homogenization. Thermal treatment was carried out at a temperature of 320°C, during 4 hours in argon atmosphere. As a result, the formation of Ni_2Zn_{11} intermetallic phase was stated [7].

In dependence on the condition of deposition process the Zn+Ni coatings contained 1-40 wt% Ni , whereas the percentage of Ni in Ni-Zn+Ni/Zn coatings varied from 20 to 56 wt%.

To investigate the corrosion resistance of the coatings the salt spray test was applied in 5% NaCl solution at a temperature of 35°C for 48 hours, using KOHLER HK 400 salt spray chamber. The appearance of tested coatings was observed after every 12 hours of test. Surface morphology of the coatings before and after salt spray test was investigated using Axiovert 40 MAT Zeiss microscope.

Phase composition of the corrosion products was determined by X-ray diffraction using Bragg-Brentano and grazing incidence X-ray diffraction (GIXD) methods.

The X-ray patterns were measured using the X'Pert Diffractometer PW 3040/60 type (PANalytical) with the copper radiation ($K_{\alpha1}$ λCu = 1.5406 Å). The grazing incident beam measurements were performed with the KDUnipress equipment. The angles of the incident beam were: α = 0.1, 0.5, 1.0, 5.0 and 10°. Phase identification were carried out basing on the ICDD PDF2 2009.

The effective penetration depth (EPD) of the X-ray radiation for the studied coatings were calculated from the equation:

$$z = \frac{-\ln(1-G_x)}{\mu\left[\dfrac{1}{\sin\alpha} + \dfrac{1}{\sin(2\theta-\alpha)}\right]}$$

(1)

where:
 z - penetration depth [μm],
 G_x - total diffraction intensity which is contributed by a surface layer of the depth z,
 μ - linear absorption coefficient,
 α - incidence angle,
 θ - Bragg angle.

Electrochemical corrosion resistance investigations of the prepared coatings were conducted in 5% NaCl solution at a room temperature, using AUTOLAB®/PGSTAT20 electrochemical system (Eco Chemie B.V. the Netherlands). The experiments were carried out in Metrohm® glass cell with the platinum counter electrode and the saturated calomel reference electrode (SCE). The potentiodynamic curves in the range of ±0.05 V to the open circuit potential, were recorded at a rate of 1mV·s^{-1}. On the base of the obtained results, the corrosion potential - Ecorr, corrosion current density - icorr and the polarization resistance - R$_p$ were determined by Stern method. These values served as a measure of the corrosion resistance of investigated coatings and were compared to the results obtained for Zn coating.

3. Results and discussion

Electrochemical corrosion resistance investigations in 5% NaCl solution were conducted for electrolytic Zn+Ni and (Zn-Ni)/Zn coatings in reference to Zn coating. On the basis of the obtained i = f(E) dependences the values of corrosion parameters were determined by Stern method (Table 1). The corrosion protection of Zn+Ni coatings is dependent on the Ni content. With the increase in the Ni percentage the value of corrosion potential becomes more positive which is accompanied by the increase in polarization resistance and the decrease in corrosion current values.

Table 1.
The corrosion parameters determined by Stern method for zinc-nickel coatings in 5% NaCl

Electrode	E_{corr} [V]	i_{corr} [μA/cm^2]	R_p [k Ω·cm^2]
Zn	-1.052±0.002	8.40±2.3	1.92±0.2
Zn*	-1.061±0.003	1.842±0.1	6.77±0.4
Zn+Ni (5%Ni)	-0.953±0.006	14.85±4.9	0.89±0.1
Zn+Ni (18%Ni)	-0.931±0.008	11.70±4.6	1.07±0.1
Zn+Ni (28%Ni)	-0.904±0.003	10.25±3.2	1.23±0.2
Zn+Ni (40%Ni)	-0.865±0.005	7.50±1.1	2.07±0.2
Zn+Ni (40%Ni)*	-0.971±0.007	3.021±0.2	3.27±0.3
(Zn-Ni)+Ni/Zn (20%Ni)	-0.812±0.006	6.05±0.3	2.23±0.2
(Zn-Ni)+Ni/Zn (43%Ni)	-0.732±0.002	2.50±0.1	1.30±0.1
(Zn-Ni)+Ni/Zn (56%Ni)	-0.746±0.003	2.36±0.2	3.91±0.4

* - the coatings after salt spray test
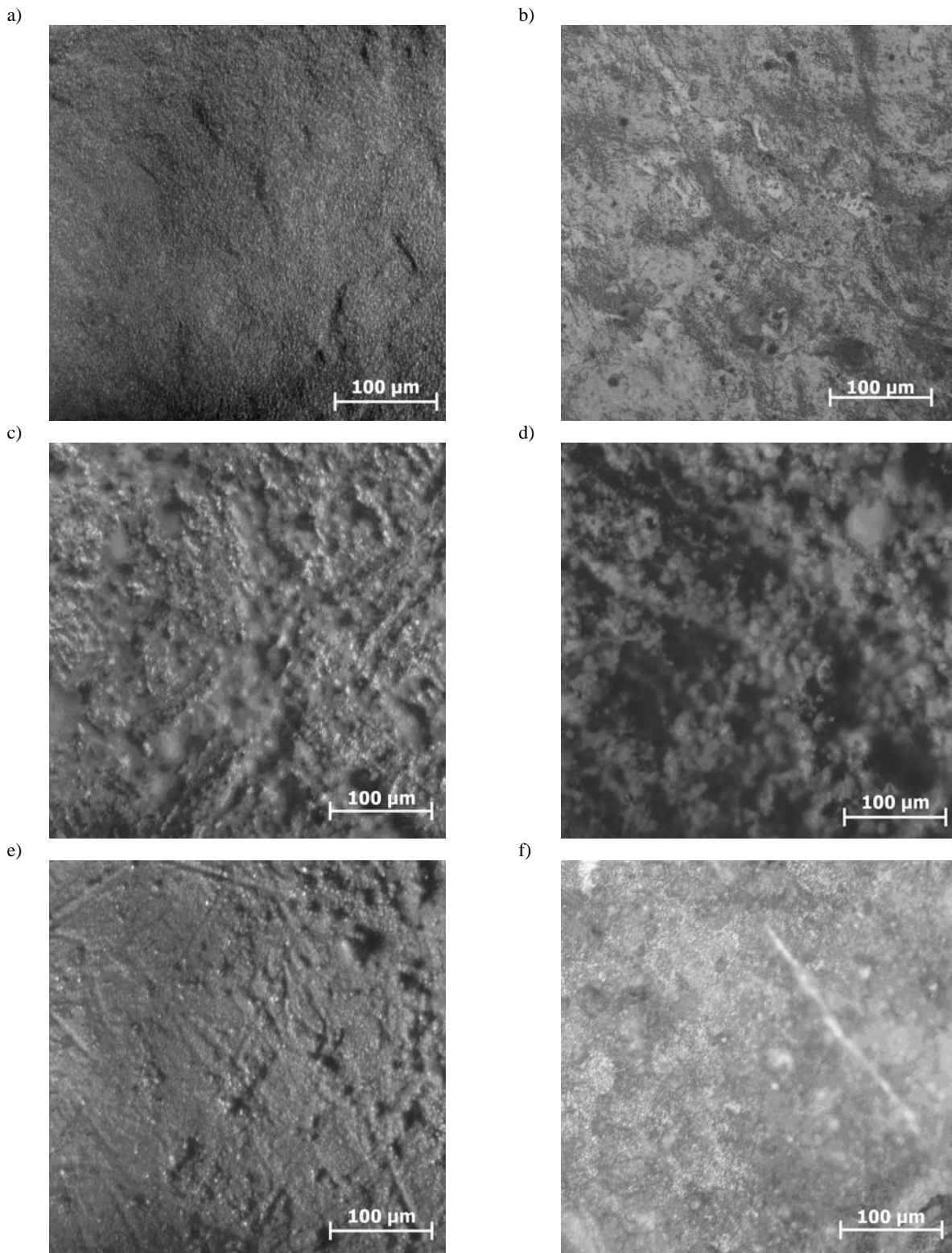
a)

b)

c)

d)

e)

f)

Fig. 1. Surface morphology of Zn coating before (a) and after (b) salt spray test, Zn+Ni40% coating before (c) and after (d) salt spray test, Ni-Zn+Ni/Zn (56%Ni) coating before (e) and after (f) salt spray test

Ni-Zn+Ni/Zn coatings contains the greater amounts of Ni compared to Zn+Ni coatings, so their corrosion resistance is higher, which is expressed by more positive potential values, lower corrosion current values and the increase in polarization resistance.

As the corrosion resistance is strongly influenced by the structure and phase composition of the examined material it could be assumed that the improvement in the corrosion protection of examined zinc-nickel coatings is related to the presence of Ni_2Zn_{11} intermetallic phase. So, the best corrosion parameters are found for the Zn+Ni and Zn-Ni/Zn above 40% Ni, where the content of this phase is the highest.

The results of salt spray test exhibit the appearance of white rust corrosion, which is characteristic for zinc oxidation process (Fig. 1). The first changes on the coatings and the appearance of white bloom attributed to corrosion processes were observed after 24 hours. However, it should be noticed, that steel substrate was well-protected by zinc-nickel coatings, as any signs of steel corrosion like red rust were observed.
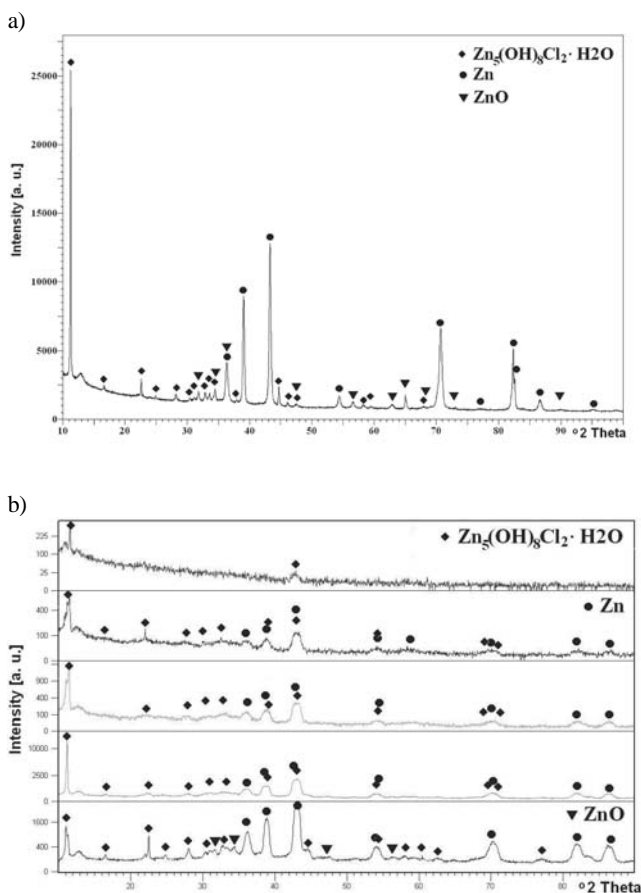
a)

b)

Fig. 2. The X-ray diffraction patterns of the Zn coating measured by a) Bragg-Brentano geometry and b) GIXD technique

Results of phase composition investigation by the X-ray diffraction method show, that the main component of corrosion products of tested coatings is $Zn_5(OH)_8Cl_2 \cdot H_2O$ phase, arising in

the consequence of zinc corrosion. The phases created as result of nickel corrosion were not found. Besides $Zn_5(OH)_8Cl_2 \cdot H_2O$ phase in both kinds of zinc-nickel coatings ZnO and Ni_2Zn_{11} phases are present. Intermetallic Ni_2Zn_{11} phase is formed during thermal treatment of zinc-nickel coatings.

The X-ray diffraction patterns measured in the Bragg-Brentano geometry show the final results of corrosion process in whole sample volume (Fig. 2a, Fig. 3a, Fig. 4a). The analysis of the diffraction patterns measured in the GIXD technique has shown that the phase composition of coatings was changed versus the penetration depth of the X-ray radiation (Fig. 2b, Fig. 3b, Fig. 4b). The main product of the corrosion process - $Zn_5(OH)_8Cl_2 \cdot H_2O$ phase was detected in Zn and Zn+Ni coatings on the depth of 3.3 and 2.1 µm, respectively (Table 2). In the Ni-Zn+Ni/Zn composite coating this phase was detected on the depth of 1.6 µm. In the bigger penetration depth of the X-ray radiation, the other phases like Zn, ZnO and Ni were detected in all samples. Their presence is the effect of the coating oxidation. Moreover, in the Ni-Zn+Ni/Zn coating the Ni_2Zn_{11} intermetallic phase was present, similar to the results obtained for Zn+Ni coatings after thermal treatment (Table 2).
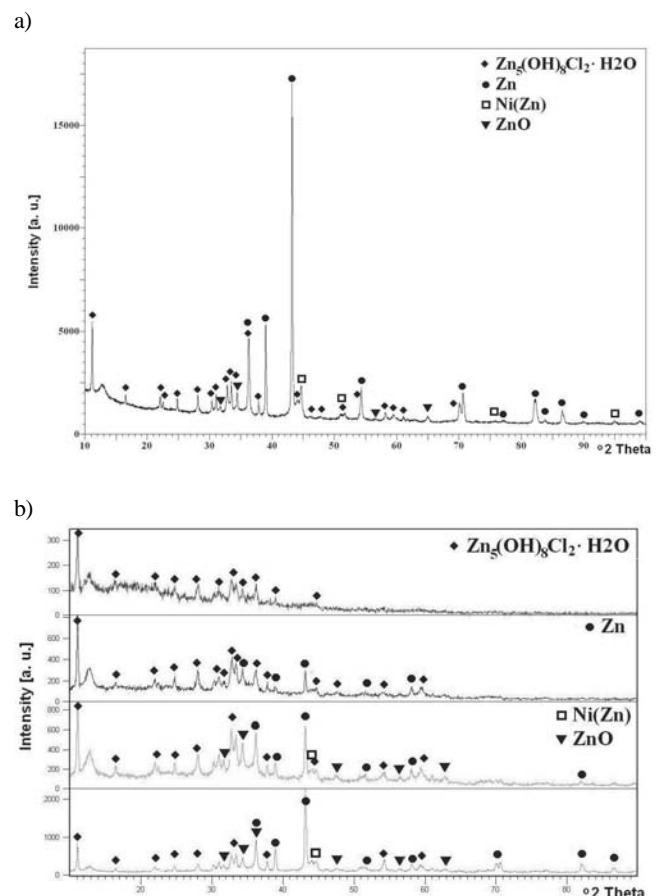
a)

b)

Fig. 3. The X-ray diffraction patterns of the Zn+ Ni coating measured by a) GIXD technique and b) Bragg-Brentano geometry

Table 2.
The phase analysis of the Zn, Zn+Ni and Ni-Zn+Ni/Zn coatings (X-ray diffraction patterns measured using the GIXD technique)

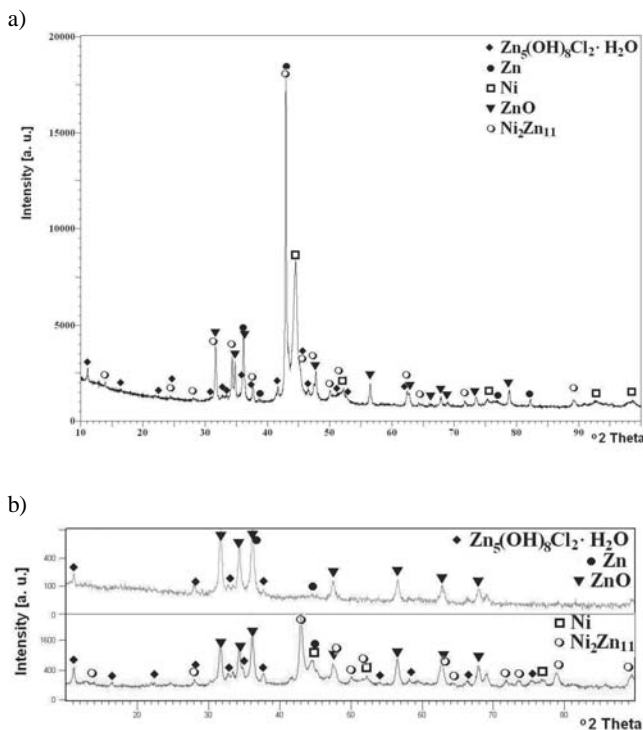| Coating	Incidence angle α [°]	Thickness [μm]	Phase analysis (ICDD PDF2 2006)
Zn	0.1	3.3	$Zn_5(OH)_8Cl_2·H_2O$
	0.5	10.6	$Zn_5(OH)_8Cl_2·H_2O + Zn$
	10.0	13.4	$Zn_5(OH)_8Cl_2·H_2O + Zn + ZnO$
Zn+Ni	0.1	2.1	$Zn_5(OH)_8Cl_2·H_2O$
	0.5	7.2	$Zn_5(OH)_8Cl_2·H_2O + Zn$
	10.0	7.8	$Zn_5(OH)_8Cl_2·H_2O + Zn + ZnO + Ni$
Ni-Zn+Ni/Zn	0.1	1.6	$Zn_5(OH)_8Cl_2·H_2O + Zn + ZnO$
	0.5	6.5	$Zn_5(OH)_8Cl_2·H_2O + ZnO + Ni + Ni_2Zn_{11}$

a)

b)

Fig. 4. The X-ray diffraction patterns of the Ni-Zn+Ni/Zn coating measured by a) Bragg-Brentano geometry and b) GIXD technique

The presence of the corrosion products on the electrode surface influences the protective properties of the examined coatings. Though corrosion potential of the Zn+Ni 40% coating after salt spray test is decreased, nevertheless lower values of corrosion current and the increase in polarization resistance point at the hindered charge transfer between the solution and the electrode surface and the inhibition of corrosion process (Table 1).

4. Conclusions

The corrosion resistance of zinc-nickel coatings is dependent on Ni content and it grows with the increase in Ni percentage in the coatings. The higher corrosion resistance could be attributed to the presence of intermetallic Ni_2Zn_{11} phase. The maximum protective ability is reached for the coatings above 40% Ni, where the content of this phase is the highest.

The results of salt spray test exhibit the appearance of white rust corrosion, which is characteristic for zinc oxidation process. The main component of corrosion products was $Zn_5(OH)_8Cl_2·H_2O$ phase. The products related to the nickel or steel substrate corrosion process were not found.

The application of the GIXD technique has allowed to determine the changes in the phase composition of the corrosion products in the zinc and zinc-nickel coatings versus the penetration depth of the X-ray radiation.

The presence of corrosion products on the electrode surface results in further improve in their protective ability and the limiting of the corrosion processes.

Acknowledgements

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